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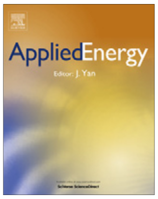

Characterization of microalga Chlorella as a fuel and its thermogravimetric behavior

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HIGHLIGHTS

- Proximate and ultimate analysis of two microalgae (*Nannochloropsis* and *Chlorella* spp.).
- TGA of *Chlorella* spp. and *Nannochloropsis* investigated at 15 °C/min up to 800 °C.
- 1.2 kg of Chlorella pyrolyzed in a novel batch, intermediate pyrolysis pilot reactor at 450 °C.
- Bio-oil from Chlorella oil analysed and compared to pine chips fast pyrolysis oil.
- Bio-oil from Chlorella exhibited superior properties compared to lignocellulosic pyrolysis oil as intermediate energy carrier.

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ABSTRACT

Microalgae are photosynthetic microorganisms living in marine or freshwater environment. In this study, samples of *Chlorella* spp. and *Nannochloropsis* from two different origins were analysed to settle a preliminary characterization of these microorganisms as intermediate energy carriers and their properties compared to a conventional lignocellulosic feedstock (pine chips). Both microalgae samples were characterized in terms of elemental composition (CHONS and P) and thermogravimetric behavior. This was investigated through non-isothermal thermogravimetric analysis in nitrogen atmosphere at heating rate of 15 °C min^{-1} and temperature up to 800 °C. Solid residues produced at 300 °C and 800 °C from TGA were also analysed to determine the ultimate composition of chars. Activation energy, reaction order and pre-exponential factor were calculated for the single step conversion mechanism of 1 g of *Chlorella* spp. and compared to literature data on *Chlorella protothecoides* and *Spirulina platensis*. Calculated kinetic parameters, given as intervals of several determinations, resulted to be: pre-exponential factor (A) 1.47–1.62E6 min^{-1}, activation energy (E) 7.13–7.92E4 J mol^{-1}, reaction order (n) 1.69–2.41. 1.2 kg of *Chlorella* spp. was then processed in a newly designed batch pyrolysis pilot reactor, capable of converting up to 1.5 kg h^{-1} of material, and pyrolysis liquid collected, analysed and compared with a sample of fast pyrolysis from pine chips. This preliminary investigation aimed at carrying out a first characterization of algae oil and optimise the operational aspects of the reactor, tested with the first time with this unconventional feedstock. The algae pyrolysis oil exhibited superior properties as intermediate energy carrier compared to pyrolysis oil from fast pyrolysis of pine chips, in particular higher HHV and carbon content and lower oxygen and water content. These data can potentially be used in the design and modelling of thermochemical conversion processes of microalgae.

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1. Introduction

Microalgae are a diverse group of prokaryotic and eukaryotic photosynthetic and heterotrophic microorganisms. Microalgae cultivation, or *algaculture*, using sunlight can be carried out in open or covered ponds or closed photo-bioreactors, based on different designs [1] and in several aqueous media, from fresh to very salty water. Nowadays more than 40 different species of microalgae, isolated in different parts of the world, are cultivated as pure strains in intensive systems. Microalgae can be extremely efficient in terms of land-use, as the potential oil productivity per hectare is considerably higher than traditional seed crops [1] and total biomass production rate (productivities) achievable with reactors is estimated at around 60–70 ton ha^{-1} $year^{-1}$ [2], but the theoretical potential is assessed to be even higher [3].

Algaculture is performed to produce high added value commodities. Sometimes the entire alga is the final product, but more often several compounds are extracted. Some examples of these so-called "unique products" include oils, fats, vegetable protein, carbohydrates, bioactive compounds and chemicals as well as food, food-additives and health-food, feed for fish, shrimp and shellfish, dyestuff and omega-3-fatty acids [4,5].

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Nomenclature

HHV	higher calorific value
LHV	lower calorific value
NF	nitrogen factor
TGA	thermogravimetric analysis
PID	proportional-integral-derivative effect

Symbols

h	hour
min	minute
Nl	normal-litre
s	second
t	time
T	temperature
α	conversion of reactant
Δ	uncertainty or finite difference

Abbreviations

ar	as received
avg	average
dry	dry base
daf	dry ash free
i	index
v/v	by volume
wt.%	percentage by weight
x	measured value

Under normal growing many species of microalgae exhibit a lipid yield between 10% and 30% on dry weight, but under special conditions the lipid content can be even doubled [6], and some Authors reported to have obtained oil content up to 80% by weight of dry biomass [7–9]. Growing of microalgae depends on the nutrients in the water as well on the illumination that is available for photosynthesis. The intake of nutrients can modify the production and accumulation rate of lipids within the microalgae. For example, Rodolfi et al. [6] reported an increased productivity and almost doubling of the lipid content to 60% after switching to nutrient-deficient conditions in an outdoor pilot reactor.

The algal biomass is a valuable source of carbon, because its content can exceed 50% on dry weight [10] and some microalgae can produce larger amount of oil than the best dedicated energy-crop and can therefore represent a potential renewable source of oil for the biofuel chains.

Several possible pathways for microalgae biomass-to-energy have been investigated, and several reviews are available in literature (such as [12–14]). Process technologies for the conversion of microalgae biomass encompass two main categories: thermochemical and biochemical processes. Thermochemical pathway includes direct combustion, gasification, liquefaction and pyrolysis, whereas the biochemical pathway includes anaerobic digestion, alcoholic fermentation. Another process option is trans-esterification, where the fatty acids can be converted into biodiesel. The scheme of Fig. 1 summarizes some of the possible conversion processes and final products.

According to the definition given by the International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermal analysis is amidst the "[...] techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed" [15]. In case of thermogravimetric analysis, the monitored property is the weight of the sample. Thermogravimetric analysis is used since the end of the XIX century for gaining knowledge on the solid state decomposition mechanism of substances because it is a tool that may provide insight regarding the kinetic workings of heterogeneous reactions, in spite of the lack of consistency among data sets that White et al. pointed out of in their paper [16]. Despite the literature on pyrolysis kinetic for many biomass species is abundant, and excellent review papers were published on the subject [17,18], only a limited number of studies involving the pyrolitic behavior of microalgae are reported in the open literature [19–22] and to date no studies were found reporting on the pyrolysis of algal biomass carried out on lab pilot scale reactors fed with sample sizes exceeding few grams.

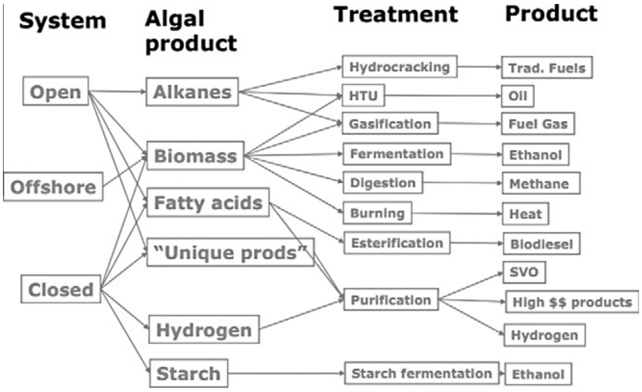

Fig. 1. Possible pathways for algae cultivation and valorisation [11].

This work aims at partially filling in the gap, by investigating the behavior of two samples of microalgae (*Chlorella* spp. and *Nannochloropsis*) during pyrolysis with a comprehensive approach. Both samples were characterized in their higher heating value (HHV) and content of carbon, hydrogen, nitrogen, oxygen, sulphur, phosphorous, moisture, ashes and their properties compared toward those of conventional lignocellulosic feedstock (pine chips). Both microalgae were then subjected to non-isothermal thermogravimetric analysis (TGA) in controlled atmosphere (nitrogen) and process condition (15 °C min^{-1}) in order to calculate kinetic parameters such as reaction order, activation energy and frequency factor, assuming the single step reaction model retained by other authors [21].

A significant amount (1.2 kg) of *Chlorella* spp. was then processed in a newly designed batch pyrolysis reactor at 450 °C and pyrolysis liquid collected, analysed and compared with a conventional sample of pyrolysis oil from fast pyrolysis of pine chips.

These data can potentially be used in the design and modelling of thermochemical conversion processes of microalgae.

2. Materials and methods

2.1. Microalgae culture and sample preparation

The microorganisms here investigated are two different batches of microalgae, *Chlorella* spp. and *Nannochloropsis*. The first sample (*Chlorella* spp.) was a proprietary strain supplied by Ingrepro B.V. (Netherland) in form of powder. The algae were grown outdoor in two separate periods of 2011 in algal ponds with 30 cm deep raceways and under outdoors climatic conditions, i.e. sunlight and natural day/night rhythm. The growing medium was enriched with potassium nitrate (KNO_3), nitrate, mono ammonium phosphate ($NH_4H_2PO_4$), phosphate, and sodium bicarbonate ($NaHCO_3$)

and pH kept constant. Microalgae were then harvested, dried, processed to obtain fine powder and shipped. The second sample was a batch of *Nannochloropsis*, grown in closed 20 l photo-bioreactor kept at 25–30 °C in F2 medium by the Hellenic Center for Marine Research (HCMR, Greece) and supplied in form of dry powder.

The two batches were received during 2011 and stored at 4 °C before analysis.

2.2. Analytical methods

Chemical and physical analyses were performed at the RE-CORD analytical laboratory according to European Norms or internal standards. Each determination was carried out in triplicate; the average of the triplicate was retained as the measured value (x_{avg}), and the uncertainty on the measurement (Δx_{avg}) was calculated as half of the difference between the maximum and minimum among the triplicates, according to the following equation:

$$\Delta x_{avg} = \frac{\max(x_i) - \min(x_i)}{2} \tag{1}$$

where $i = 1 \ldots n$ indicates replicates of the measurement and x stands for measured value. Analytical determinations were performed on a "as received" basis (ar), i.e. with the moisture content determined by equilibrium conditions with the storage environment; conversions to "dry" or "dry-ash-free" (daf) where performed according to UNI CEN/TS 15296.

2.2.1. Compositional analysis

Quantification of main components of *Chlorella* spp. was carried out by the microalgae producer (Ingrepro B.V.) and here given as average of the measured values during a whole year: thus, a composition representative of the average production. Carbohydrate, total lipids and fibers were measured by Ingrepro by Soxhlet-extract method (lipid), and phenol–sulphuric acid method (carbohydrate), whereas fibers were calculated by difference.

Protein fraction for *Chlorella* spp. was estimated from the measured nitrogen content (wt.%) of the biomass using a nitrogen factor (NF) equal to 4.78 [23]. Protein fraction was calculated as follows:

$$\text{wt.\%}_{\text{protein}} = \text{NF} \times \text{wt.\%}_{\text{N}} \tag{2}$$

2.2.2. Proximate analysis

Moisture was determined in a Leco TGA 701 instrument according to EN 14774-3 by heating at 105 °C and holding until the sample achieved a constant weight. Ashes were determined with the same instrument according to EN 14776 for solid biofuels, by heating the sample under constant air flow up to 550 °C and holding there for 2.5 h.

2.2.3. Ultimate analysis

The content in carbon, hydrogen, nitrogen and sulphur (CHN+S) was determined through a Leco TruSpec for carbon, hydrogen and nitrogen and a TruSpec Add-On Module for sulphur according to an internal lab method. A sample of about 0.080 g was weighed with a precision of 0.1 mg in a tin foil cup (Leco). The tin foil cup was twisted to seal and then placed in the carousel of the instrument. In the method, carbon, hydrogen, and nitrogen are simultaneously determined as gaseous products (carbon dioxide, water vapor, and nitrogen). For the determination of sulphur, a sample of about 80 mg was weighted with a precision of 0.1 mg in a crucible (combustion boat) and then placed in the combustion system, which was regulated at 1350 °C and fed with pure oxygen (99,99%). The sample contained in the combustion boat undergoes an oxidative-reduction process in which sulphur oxidizes to form sulphur dioxide. The accuracies of the determination were as follows: carbon ±25 ppm, hydrogen ±100 ppm, nitrogen ±40 ppm, sulphur ±5 ppm.

The phosphorous (P) content was determined according to the EN 15290:2011, Part A. 50 mg of homogenised sample were mixed with 3.0 ml H_2O_2 (30% v/v) and 5.0 ml HNO_3 (65% v/v) in a closed decomposition vessel. An adequate reaction time of was kept before closing the vessel.

The sample was digested following the heating programmes:

(1) Resistance heating:
   Step 1: Ramp to 220 °C over 1 h.
   Step 2: Hold for 1 h at 220 °C.
(2) Microwave heating
   Step 1: Ramp to 190 °C over 15 min.
   Step 2: Hold for 20 min at 190 °C.

After cooling, the digested material was then transferred into a volumetric flask. The digestion vessel was rinsed carefully and the rinse solution transferred to the volumetric flask. Deionised water was added to the digest to an appropriate volume (100 ml). The phosphorous content was determinate by ion chromatography. The solution obtained from the digestion was filtered using a syringe equipped with a 0,45 μm pore size filter tip an injected in the ion chromatograph.

Oxygen (dry basis) is estimated by difference as per the following equation:

$$\text{wt.\%}_{\text{O}} = 100 - (\text{wt.\%}_{\text{C}} + \text{wt.\%}_{\text{H}} + \text{wt.\%}_{\text{N}} + \text{wt.\%}_{\text{S}} + \text{wt.\%}_{\text{ash}} + \text{wt.\%}_{\text{P}} \tag{3}$$

2.2.4. Determination of the higher calorific value

Higher heating value was measured according to EN 14918 by means of a Leco AC500 isoperibol calorimeter. A sample of about 1 g was weighed with a precision of 0.1 mg in a crucible, then the crucible and a nickel ignition wire were placed into the calorimeter. The equipment was closed and pressurized to 29 bar with high purity oxygen (99,999%), then settled into the bucket, which was previously filled with a fixed volume of distilled water. After a suitable period required to reach thermal equilibrium, the ignition was automatically started and temperature was measured by means of an electronic thermometer with an accuracy of 0.0001 °C. The higher heating value automatically calculated by the instrument is then corrected accounting for the residual length of the nickel wire.

2.3. Viscosity

Kinematic viscosity of pyrolysis oil was measured with a Lauda viscometer made by an Ubbelohde capillary tube controlled by iVisc software and a Proline PV 15 thermostatic bath filled with deionized water. Sample was introduced in the capillary tube and allowed to reach the selected temperature in the thermostatic bath before starting the analysis. Each measurement was carried out at the selected temperature for five times: two times in order to precondition the capillary tube, then the last three times for analyses: an interval of 90 s occurred between every measurement.

2.4. Thermogravimetric analysis

The algal cells were analysed in pyrolytic conditions by means of a Leco TGA 701 instrument in a nitrogen atmosphere. All the thermogravimetric analyses (TGA) were conducted under a flow of 8.5 l min^{-1} of high purity nitrogen gas (99,999%) in order to prevent the oxidation of the samples. Samples of algal cells were heated from room temperature to 800 °C at oven heating rates of

15 °C min^{-1} in porcelain crucibles held by a pneumatic carousel; only one crucible was loaded into the carousel at a time, and each TGA test was repeated in triplicates. The temperature of the oven was measured with a precision of ±2% of the reading. Weight loss of each sample was recorded about every 2 min with a precision of ±1E−4 g and subjected to an automatic correction according to the nitrogen density variation as the temperature was increased from ambient to 800 °C. Records of weight loss of each sample were collected to determine both thermogravimetric (TG) and derivative thermogravimetric (DTG) curves. Three series of independent tests were carried out in triplicates with about 1 g of *Chlorella* spp. and 100 mg of both *Chlorella* spp. and S2 and *Nannochloropsis*.

2.5. Determination of the kinetic parameters

In this study, the Freeman–Carroll method [24] was adopted to infer the values of pre-exponential factor (A, min^{-1}), activation energy (E, J mol^{-1}) and reaction order (n) from the TGA plot according to the procedure adopted by Peng et al. [21].

Let α be the conversion of reactant expressed as follows:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{4}$$

where m is the mass of the sample at time t and pedix 0 and ∞ refers to the initial and final mass respectively.

A generic decomposition reaction can be expressed as follows:

$$\frac{d\alpha}{dt} = A(1-\alpha)^n e^{-\frac{E}{RT}} \tag{5}$$

where t is the time, T the temperature (K), R the universal gas constant (8.34 J·(K mol)$^{-1}$). For a non-isothermal process with constant heating rate $dT\,dt^{-1} = \beta = 15$ °C min≈, we have:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1-\alpha)^n e^{-\frac{E}{RT}} \tag{6}$$

Indicating with Δ the difference between two measurement, for the corresponding α and T it is possible to calculate E and n from a plot of $\Delta\ln(d\alpha\, dT^{-1})/\Delta\ln(1-\alpha)$ versus $\Delta(T^{-1})/\Delta\ln(1-\alpha)$ that gives a straight line with slope of $-(E\,R^{-1})$ and intercept n. It is then possible to calculate A by substituting back E and n in Eq. (6) along with the values of T, α, and $d\alpha\, dT^{-1}$.

Data were analysed with Excel 2011 for Mac by Microsoft Corporation.

2.6. Batch pyrolysis reactor

For this study, a new batch pyrolysis reactor jointly developed by CREAR-University of Florence (Florene, Italy) and SEA Marconi Technologies (Turin, Italy) and capable of converting up to 1.5 kg h^{-1} of material was used for processing microalgae to obtain a pyrolysis liquid. The reactor consists of a cylindrical body of corrosion resistant stainless steel (AISI 310) externally heated by two ceramic-shell electrical resistors and capable of maintaining the reactive environment up to 600 °C; mixing of the feedstock is promoted by a variable speed stirrer and reactor temperature is measured at the stirrer end by means of a K type thermocouple. The reactor features three openings: one is for biomass loading (that can be performed anytime during operation), one for continuous vapor discharging and the last for discontinuous, manually operated, solid residue removal. Vapors are cooled down in the condenser, separating in a pyrolysis liquid that is condensed and collected and a mixture of permanent gases that are vented outside by an ATEX-certified blower. A PID (proportional-integral-derivative) controller regulates process temperature; data acquisition is performed continuously. A schematic of the reactor is reported in Fig. 2.

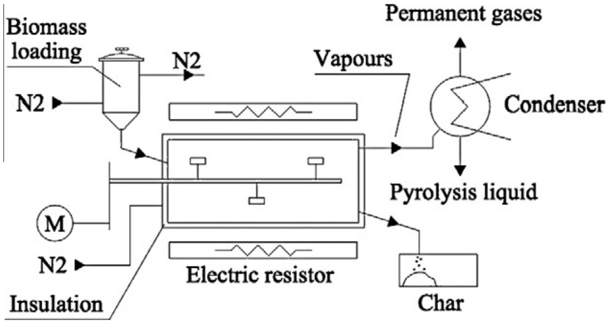

Fig. 2. Schematic of the batch pyrolysis reactor.

The test procedure is carried out as follows: the empty reactor is heated up to the desired process temperature under a constant nitrogen flow of 4 Nl min^{-1} and then the feedstock is inserted from one end in batches of 20–40 g; prior to loading the biomass into the reactor, the material is washed for 30 s with nitrogen to avoid oxygen entrance into the process. During the test, the PID regulates the power supplied to the resistors to keep the process temperature constant. Once the material is completely processed, the stirrer is stopped and solid discharge port opens to un-load the reactor from solid residue (char). The solid is collected in a closed vessel filled with nitrogen, and let cool down to room temperature.

3. Results

3.1. Microalgae composition

Compositions of microalgae samples were determined in terms of proximate and ultimate analysis. Results of the determinations for both samples are reported in Tables 1 and 2, along with data for pine chips, which were retained in this study as the reference lignocellulosic biomass. Protein content was inferred by the elemental nitrogen concentration, whereas average data for carbohydrate, lipid and fibers content for *Chlorella* spp. were supplied by Ingrepro B.V. No data about the compositional analysis of *Nannochloropsis* where made available.

Both microalgae resulted very rich in ash content, 21.6% dry base and 13.2% for *Chlorella* spp. and *Nannochloropsis* respectively, compared to the very low ash content of pine chips (0.4 wt.% dry). To determine the influence on the ash content of the nutrients in the growing media, *Chlorella* spp. was washed in demineralized water before carrying out a second analysis, yielding to a lower ash concentration (17.6% dry). Also considering the washed microalga, the measured ash content resulted to be several times higher than what could be found in literature for similar microalgae strains (5.83 wt.% ar as reported by Phukan et al. [31]); this aspect will need further investigation to determine the effect of growing condition on the ash content of *Chlorella* spp. The high ash content limits the energy density by mass of microalgae and could represent a problem if the biomass is directly fed to a burner; anyhow, a preliminary test carried out with an ash-melting oven on ashes from *Chlorella* spp. sample showed that at least up to 1700 °C no evidence of ash melting could be detected.

Both *Chlorella* spp. and *Nannochloropsis* exhibited a carbon and hydrogen content almost identical to that of pine chips, whereas significant differences were found in nitrogen and oxygen content. Nitrogen is almost absent in lignocellulosic biomass, whereas a significant content could be found in both microalgae, 6.7 wt.% and 7.5 wt.% dry base for *Chlorella* spp. and *Nannochloropsis* respectively, due to the presence of proteins in microalgae; the high nitrogen content can be a limiting factor for the use of microalgae in combustion systems being a source of fuel-NOx and thus

Table 1
Proximate and compositional analyses of *Chlorella* samples S1 and S2 and reference lignocellulosic feedstock (pine chips).

Feedstock	Proximate analysis		Compositional analysis			
	Moisture (wt.% ar)	Ash (wt.% dry)	Protein (wt.% ar)	Carbohydrates (wt.% ar)	Lipid (wt.% ar)	Fibers (wt.% ar)
Chlorella spp.	6.2	21.6	29.6	15–16.5[a]	9–13[a]	5–15[a]
Nannochloropsis	6.0	13.2	–	–	–	–
Pine chips	5[b]	0.4[b]	–	–	–	–

[a] Data supplied by the microalgae producer (Ingrepro B.V., The Netherland) as average on the year and representative of their products.
[b] Data provided by Biomass Technology Group (BTG – The Netherland) from analytical determinations.

Table 2
Ultimate analysis and higher calorific value of *Chlorella* spp., *Nannocloropsis* and pine chips.

Parameter	*Chlorella* spp.	*Nannochl.*	Pine chips[b]
Carbon (wt.% dry)	46.1	48.2	49.3
Hydrogen (wt.% dry)	6.1	6.9	6.3
Nitrogen (wt.% dry)	6.7	7.5	0.01
Sulphur (wt.% dry)	0.4	0.4	<0.01
Oxygen[a] (wt.% dry)	19.1	23.2	44.1
Phosphorous (wt.% dry)	1.6	0.6	–
O/C	0.41	0.48	0.89
H/C	0.13	0.14	0.13
HHV[c] (dry, MJ kg^{-1})	20.4	21.7	19.2
HHV (dry, MJ kg^{-1})	19.5	22.2	–

[a] Calculated by difference according to Eq. (3).
[b] Data provided by Biomass Technology Group (BTG), The Netherland.
[c] wt.% dry, Calculated according to the Milne formula.

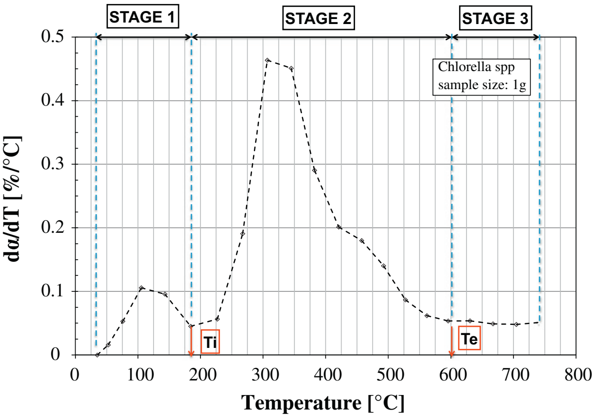

Fig. 3. Plot of the discrete derivative of the conversion of reactant (Eq. (4)) with respect to temperature ($d\alpha\ dT^{-1}$) versus temperature of *Chlorella* sample S1 during pyrolysis in inert atmosphere at heating rate of 15 °C min^{-1} (1 g sample mass), with highlighted the different devolatilization stages.

requiring the adoption of proper gas cleaning and/or catalytic treatment systems of the flue gas.

The oxygen content of both microorganisms resulted to be almost half of pine, due to the combined effect of high nitrogen and ash content of microalgae.

The energetic value of *Chlorella* spp. and *Nannochloropsis*, on a dry base, resulted to be comparable to that of pine chips; this aspect can be explained by taking into account the contribution of lipids, which have a high energetic content and are absent in lignocellulosic specie like pine.

3.2. Thermogravimetric analysis

3.2.1. Large sample (1 g)

A first run of TGA test was carried out on 1 g of *Chlorella* spp. to determine its kinetic parameters (activation energy, pre-exponential factor and reaction order) assuming the same single step conversion mechanism retained by other Authors [21]. In our tests, 1 g of *Chlorella* spp. was loaded into the thermogravimetric analyser, subjected to non-isothermal pyrolysis and its weight loss versus time and temperature recorded; in this test, the oven was programmed to obtain an heating rate of 15 °C min^{-1} up to a final temperature of 800 °C. It should be noted, however, that the heating rate of the sample was not measured directly and deviation may occurs between the heating rate of the oven and that of the sample.

Fig. 3 reports the plot of conversion of reactants (α) as a function of temperature for *Chlorella* spp. It can be observed that the pyrolysis of *Chlorella* spp. undergoes three main devolatilization phases: the first phase (stage 1) begins at room temperature and ends at about 180 °C; during this stage, moisture is released from the carbonaceous matrix and a weight loss of about 6.87% is measured. In the second phase (stage 2) the main devolatilization occurs and the pyrolysis takes place. In this phase, the weight loss is markedly higher compared to stage 1 and the reaction proceeds with an increased velocity, as indicated by the plot, which has a maximum rate at about 307 °C between Ti (185 °C) and Te (596 °C). During stage 2 *Chlorella* spp. attains a weight loss of about 55%. Ti was assumed as the intermediate minimum between the peaks of stage 1 and 2, whereas Te was taken as the temperature at which the value of the temperature derivative of the conversion of reactants is equal to those calculated at Ti [25]. In the third phase (stage 3) the solid carbonaceous material undergoes a slow but constant degradation after the completion of the main devolatilization process, without reaching an asymptotic value before the end of the test.

3.2.2. Small sample (100 mg)

With the aim of gaining a better understanding of the behavior of *Chlorella* and *Nannochloropsis* during pyrolysis, another set of TGA experiments were carried out under the same oven heating rate of 15 °C min^{-1}, but with a reduced sample mass (100 mg) and extended final temperature; it was decided to reduce the mass of the sample in the crucible of the thermogravimetric analyser to limit the temperature difference between the oven (reactive environment) and the sample, with the aim of reducing the difference between imposed (oven) and actual (sample) heating rate. Results of these tests are presented in Fig. 4a and b, where the residual sample mass (%) and the discrete time derivative of the residual mass (% min^{-1}) are plotted against temperature for both *Chlorella* spp. and *Nannochloropsis*.

Apart from moisture, that is released just before attaining 100 °C, both DTG plots highlight that after the main devolatilization peak, which appears just before attaining 300 °C, a second devolatilization region appears over a wide temperature interval (400–700 °C). This second stage exhibits a lower intensity when compared to the first one, and its distribution over temperature depends on the microalgae specie: for *Chlorella* spp., the second peak is concentrated between 400 and 650 °C (with a significant overlap with stage I); for *Nannochloropsis*, the second peak is spread over a wider interval, i.e. between 400 and 730 °C. The first devolatilization stage is

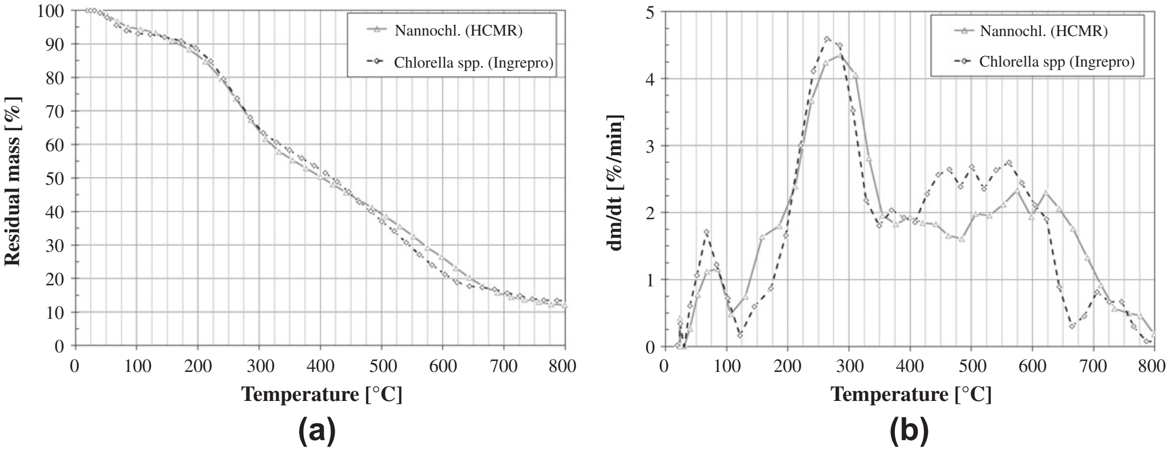

Fig. 4. Plot of the TGA (a) and DTG (A) curves for 100 mg of *Nannochloropsis* (solid grey line) and *Chlorella* spp. (dashed black line) under the heating rate of 15 °C min^{-1}. *dm dt*$^{-1}$ is the discrete derivative of the residual mass with respect to time.

generally attributed to carbohydrate and protein devolatilization, whereas the second stage was related by some Authors to lipids [20] but it was also proposed a connection with mineral matter decomposition [26]. Only with *Chlorella* spp. a third devolatilization rate peak, markedly less intense, appeared in the interval 650–800 °C and led to a complete conversion of the material, as indicated by the TGA plots of Fig. 4. This third peak is supposed to be linked to the solid residue (char) devolatilization [21,26,27]; for *Nannochloropsis*, the solid residue devolatilization (third peak) cannot be isolated from the second one.

3.3. Analysis of the char

In order to investigate in the conversion of solid residue (char) during TGA (as previously described), an essay was carried out in which a microalgae sample of about 100 mg was subjected to thermogravimetric analysis under the usual conditions (15 °C min^{-1} and nitrogen atmosphere) up to approx. 350 °C and then cooled down to room temperature (interrupted TGA). Once cold, the sample was removed from the thermobalance and analysed in its elemental composition (CHNS and P). The analysis was also performed on the solid residue at the end of the complete TGA reported in Section 3.2.2 and results are reported in Table 3.

From the analysis of Table 4 it can be seen that for both species, the char residue at 330 °C retain almost the same composition of the untreated microalgae, i.e. CHNS+P compositions do not largely differs; it is worth to note that at this temperature, which is comparable to a severe torrefaction but with higher mass loss (compared to lignocellulosic biomass), phosphorous remains fixed to the char.

A major changing in residue composition only takes place during the third stage of conversion and further studies will be needed to investigate this aspect by sampling the char between 330 and 900 °C.

3.4. Calculated kinetic parameters for large sample (1 g) of Chlorella spp.

Based on the DTG curve of Fig. 3 the kinetic parameters of Eq. (5) can be calculated according to the procedure described in Section 2. Results are reported in Table 4, along with corresponding values from the work of Peng et al. [21] on *Chlorella prothotecoides* and *Spirulina platensis* under the same heating rate (15 °C min^{-1}).

Calculated parameters are reported as interval of values from different data set; as it can be seen, the amplitude of the range is less than 10% of the corresponding maximum for both A and E, whereas the calculated values of reaction order (n) suffers of a larger difference. Nevertheless, the agreement with literature is quite satisfying.

3.5. Result of preliminary pyrolysis test in the batch reactor

1.2 kg of *Chlorella* powder was processed at 450 °C in the batch pyrolysis reactor described in Section 2; microalgae were loaded every 3 min in batches of up to 40 g, allowing 30 s of nitrogen purging of the material being fed to the reactor. After the sample entered the system, a sudden rise of the reactor pressure was experienced, and vapors began flowing to the condenser after approx. 4 s; after 30 s from loading, the vast majority of the vapors was evacuated and no observable overpressure could be noticed. Pyrolysis liquid was collected continuously. After testing, pyrolysis liquid was removed from the condensation unit and weighted; the reactor was then cooled down overnight and discharged from char,

Table 3
Ultimate analysis of residues from intermediate and complete TGA of *Chlorella* spp. and *Nannocloropsis*.

Parameter	*Chlorella* spp.	*Nannochl.*	*Chlorella* spp.	*Nannochl.*	*Chlorella* spp.	*Nannochl.*
Temperature (°C)	25	25	330	330	900	900
Residual weight (wt.% ar)	100	100	53.7	53.5	13	10.7
Carbon (wt.% dry)	46.1	48.2	51.85	56.20	3.48	8.31
Hydrogen (wt.% dry)	6.1	6.9	4.01	4.53	0.11	0.18
Nitrogen (wt.% dry)	6.7	7.5	7.49	8.5	0.070	0.51
Sulphur (wt.% dry)	0.4	0.4	0.036	0.853	0.2	0.3
(Oxygen + Ashes)[a] (wt.% dry)	19.1 + 21.6	23.2 + 13.2	36.6	29.9	96.1	90.7
Phosphorous (wt.% dry)	1.6	0.6	2.77	2.19	0.59	1.23

[a] Calculated by difference.

Table 4
Calculated kinetic parameters for *Chlorella* an comparison with literature results for *Chlorella prothotecoides* and *Spirulina platensis* under the same heating rate (15 °C/min).

Kinetic parameters		Present work	Peng et al. [21]
A	min^{-1}	1.47–1.62E6	1.11E4–9.16E7
E	$J\ mol^{-1}$	7.13–7.92E4	5.2–9.7E4
n	–	1.69–2.41	1.88–1.98

Table 5
Product distribution from the intermediate pyrolysis of *Chlorella* spp. at 450 °C in the batch pyrolysis reactor.

Product	Yield (wt.% ar)
Liquid	34
Char	29
Gas[a]	37

[a] By difference.

Table 6
Result from the analysis of pyrolysis oil from *Chlorella* spp. sample processed at 450 °C and pyrolysis oil from pine produced by BTG.

		S2 oil (*top*)	S2 oil (*bottom*)	BTG pyrolysis oil
Determination		Microalgae	Microalgae	Pine chips
Elemental analysis				
Carbon	wt.%	54.4 ± 1.7	10.6 ± 0.2	38.9 ± 0.4
Hydrogen	wt.%	9.6 ± 0.2	9.8 ± 0.1	7.4 ± 0.06
Nitrogen	wt.%	7.3 ± 0.3	5.7 ± 0.05	<0.01
Sulphur	wt.%	0.2 ± 0.0	<0.01	<0.01
Oxygen[a]	wt.%	28.2 ± 2.1	73.9 ± 0.4	53.7 ± 0.5
O/C	–	0.52	6.95	1.38
H/C	–	0.18	0.92	0.19
Ash	wt.%	0.45	0.05	0.06
Water content	wt.%	17.9 ± 0.8	80.4 ± 0.1	22.5 ± 0.03
HHV	$MJ\ kg^{-1}$	29.8 ± 0.8	4.4 ± 0.05	17.4 ± 0.2
Density	$kg\ (dm^3)^{-1}$	≈1	≈1.1	1.1–1.2
Viscosity@20 °C	cSt	–[b]	1.56	65.1
Viscosity@40 °C	cSt	43.2	1.08	20
Viscosity@50 °C	cSt	30.6	–	
Viscosity@60 °C	cSt	19.1	0.74	
pH	–	9.6	9.5	2.3

[a] Calculated by difference.

[b] At 20 °C the fluid was too viscous to be measured with an Ubbelohde capillary with $k = 0.3$.

which was also collected and weighted. Pyrolysis gases were calculated by difference, and product distribution by mass is reported in Table 5.

During this first test campaign it was possible to produce roughly 34 wt.% pyrolysis liquid from *Chlorella* spp.; commercial technologies showed that it is possible to attain yield of pyrolysis oil up to 60–70 wt.% from lignocellulosic materials in fast pyrolysis reactors [28–30], thus suggesting that improvement of the conversion effectiveness are possible. Oil yield from pyrolysis of lignocellulosic feeedstock is strongly dependent, among others, on process temperature and heating rate. In this preliminary study using the pilot reactor, only one temperature condition and one heating rate was investigated. In fact, the present research work aims at gathering the first indications on process pyrolysis in the pilot reactor. A systematic study on the effect of process temperature and heating rate on the oil yield from intermediate pyrolysis of microalgae will be investigated in a future research work.

The collected pyrolysis liquid exhibited separated in two phases, as reported in Fig. 5; upper phase was named S2 oil (*top*), the lower one S2 oil (*bottom*). Ultimate analysis and calorific values of both phases were determined and compared with a commercial pyrolysis oil from fast pyrolysis of pine chips produced by BTG in their proprietary rotating cone reactor [28]; results from analytical determinations are reported in Table 6. On the contrary to what generally happens with lignocellulosic biomass, where during the condensation of pyrolysis vapors a sort of water phase tends to float over the oily one, the condensation of pyrolysis vapors from microalgae led to the formation of an upper phase made by pyrolysis oil and a water-rich lower phase (water content was approx. 70 wt.%). The two phases showed different densities, approx. 1 $kg{\cdot}(dm^3)^{-1}$ for the upper phase (pyrolysis oil) and 1.1 $kg{\cdot}(dm^3)^{-1}$ for the lower one (water-rich). The different composition of the two separated phases is clearly highlighted by the measured calorific value of the upper phase (28.4 $MJ\ kg^{-1}$) that is almost six times higher than that corresponding to the lower phase (4.6 $MJ\ kg^{-1}$).

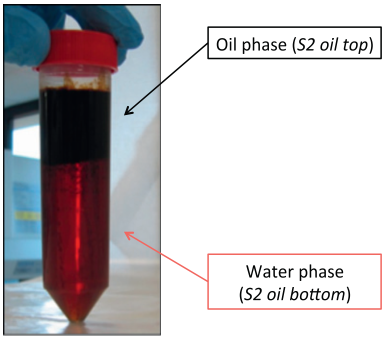

Fig. 5. Sample of the pyrolysis liquid collected from intermediate pyrolysis of *Chlorella* S2 processed at 450 °C. The oily phase S2 oil (*top*) floats on the water-rich phase S2 oil (*bottom*).

Compared to a sample of commercial pyrolysis oil from fast pyrolysis of pine chips, the upper phase exhibited very peculiar characteristics, because it was less oxygenated (approx. 35 vs. 54 wt.%), had higher HHV (28.4 vs. 17.2 $MJ\ kg^{-1}$), lower acidity (measured by the pH, 9.2 vs. 2.3 for pine chips pyrolysis oil), lower density (1 vs. 1.1–1.2 $kg{\cdot}(m^3)^{-1}$) and the its H/C ratio was closer to that of conventional automotive-grade diesel (0.15). Water content of S2 oil (*top*) was found to be comparable to that of BTG oil, the ash content was markedly higher (0.45 vs 0.06 wt.%) than the and also the nitrogen concentration was higher than the BTG oil.

The high ash content of the oil can be probably due to the presence of fine char in the oil. Fine char is produced in the reactor mainly because of the very small particle size of the microalgae powder and a very high ash content, which was determined to be approx. 56 wt.% on a dry base, characterizes it. Some of the char is entrained by the gas flow outside of the reactor and part of this powder is not completely blocked by the glass fiber filter that is installed before the vapors condensation.

Nitrogen concentration in the oil is almost the same as in the raw feedstock, which can be a limiting factor for its direct use in energy conversion systems due to NO_x formation during combustion.

4. Conclusions

In this work, the pyrolysis behavior of two microalgae batches (*Chlorella* spp. and *Nannochloropsis*) were investigated by means of chemical, physical, thermogravimetric analysis and intermediate pyrolysis in a batch reactor.

A 1 g sample of *Chlorella* spp. was subjected to thermogravimetric analysis in inert atmosphere at heating rate of 15 $°C\ min^{-1}$. It was found that *Chlorella* spp. exhibits a first devolatilization stage between ambient temperature and 185 °C, in which moisture is expelled from the carbonaceous matrix, followed by the main devolatilization stage (pyrolysis). The temperature interval in which the main devolatilization occurs was identified between 185° and 596 °C. Kinetic parameters were calculated for the main devolatilization peak (stage II), showing reasonable agreement with literature.

A TGA analysis was performed on approx. 100 mg of both *Chlorella* spp. and *Nannochloropsis* under the same process conditions to determine the effect of sample size on their behavior during pyrolysis. It was found that in both DTG plots, after the main devolatilization peak, which appears near 280 °C and is related to protein and carbohydrates, a second devolatilization stage, probably related to lipids, appears: it is distributed over a wide temperature interval (400–625 °C) and exhibits a somewhat lower intensity. A third devolatilization, markedly less intense, could be distinguished in the pyrolysis of *Chlorella* spp. in the interval 650–800 °C, corresponding to a complete devolatilization of the material. This third peak is supposed to be linked to the solid residue (char) devolatilization, but further studies need to be carried out for a better understanding of this specific aspect.

1.2 kg of *Chlorella* sample S2 was processed in a batch pyrolysis reactor at 450 °C obtaining a yield of 34 wt.% pyrolysis liquid, 29 wt.% char and 37 wt.% gases (calculated by difference). Pyrolysis vapors resulting from the process were condensed and liquid pyrolysis oil collected, analysed and compared to pine chips fast pyrolysis oil. Pyrolysis oil from *Chlorella* (upper phase) exhibits very peculiar characteristics, because it is less oxygenated (approx. oxygen content of 35 vs. 54 wt.% of conventional lignocellulosic pyrolysis oil), it has higher HHV (28.4 vs. 17.2 $\mathrm{MJ \cdot kg^{-1}}$), lower acidity (pH 9.2 vs 2.3) and lower density (1 vs. 1.1–1.2 $\mathrm{kg\,m^{-3}}$), and its H/C ratio (0.18 vs. 0.19) is closer to that of conventional automotive-grade diesel (0.15). On the other hand, the water content is comparable, the ash content is markedly higher, probably due to the presence of fine char in the oil, and the nitrogen content is almost the same as the raw feedstock, which can be a limiting factor for its direct use in energy conversion systems due to NO_x formation during combustion.

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